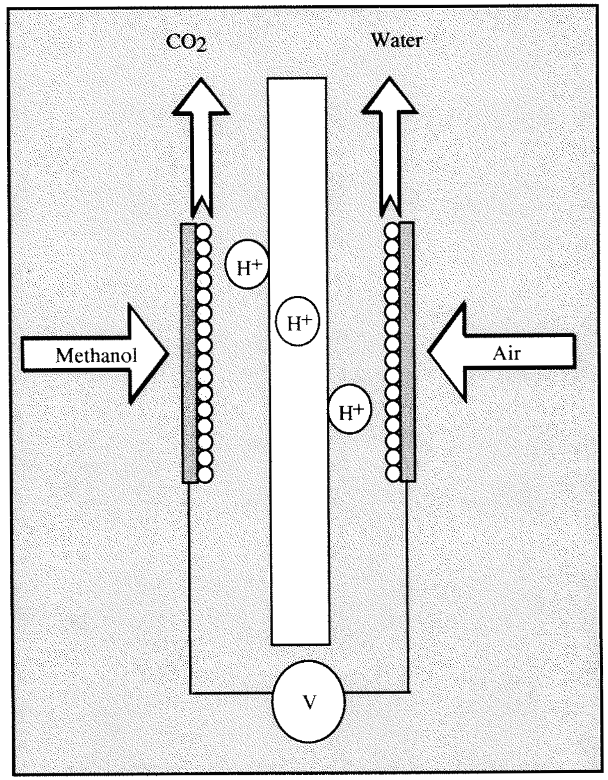
DMFC DEVELOPMENT PROGRAM

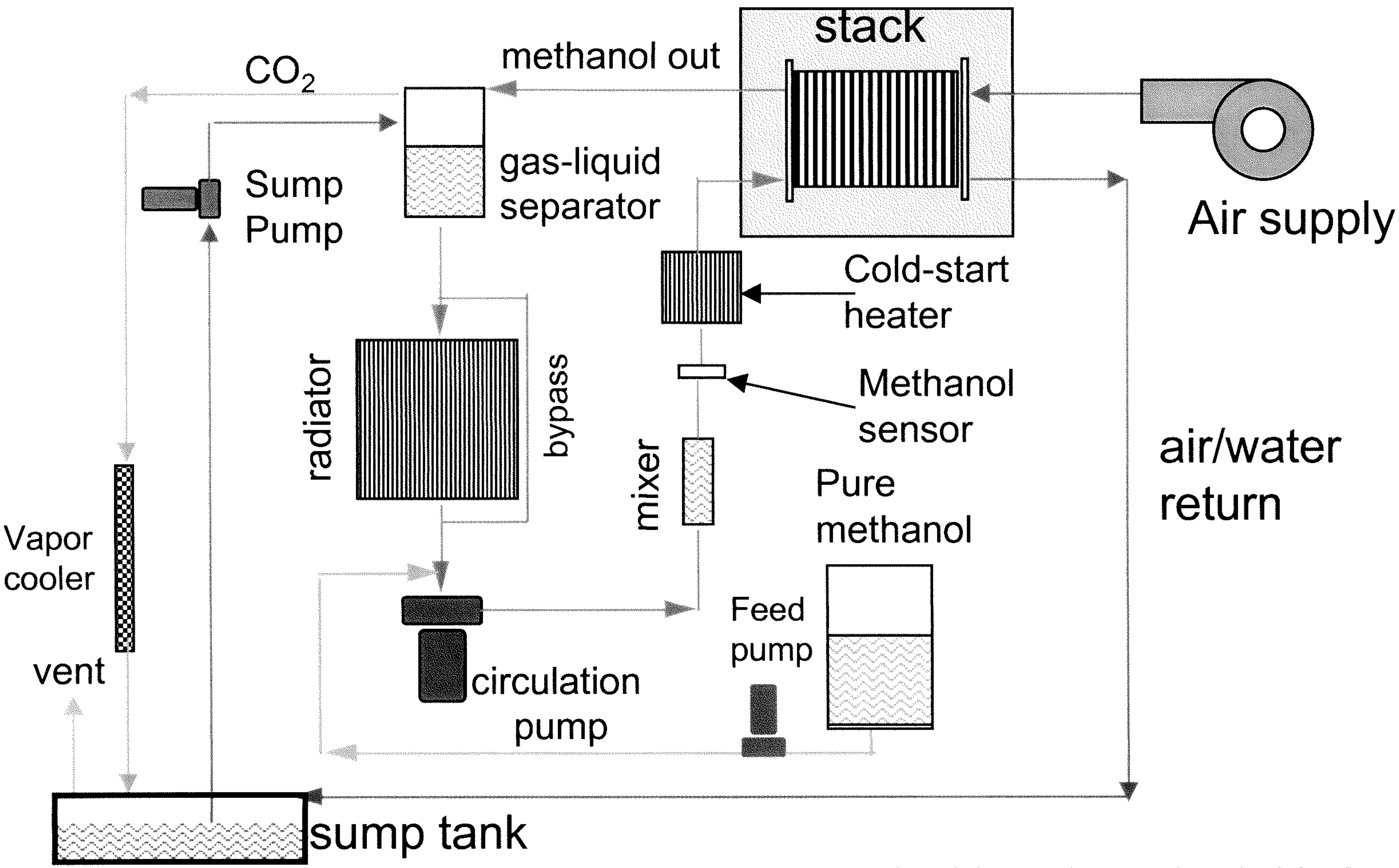
- DARPA and ARO funded effort
- 150 W Portable DMFC Power System for DOD applications
  - Materials
  - Membrane-Electrode Assemblies
  - Stacks
  - Integrated Packaged Power Source

INTRINSIC ADVANTAGES FOR SYSTEM DESIGN

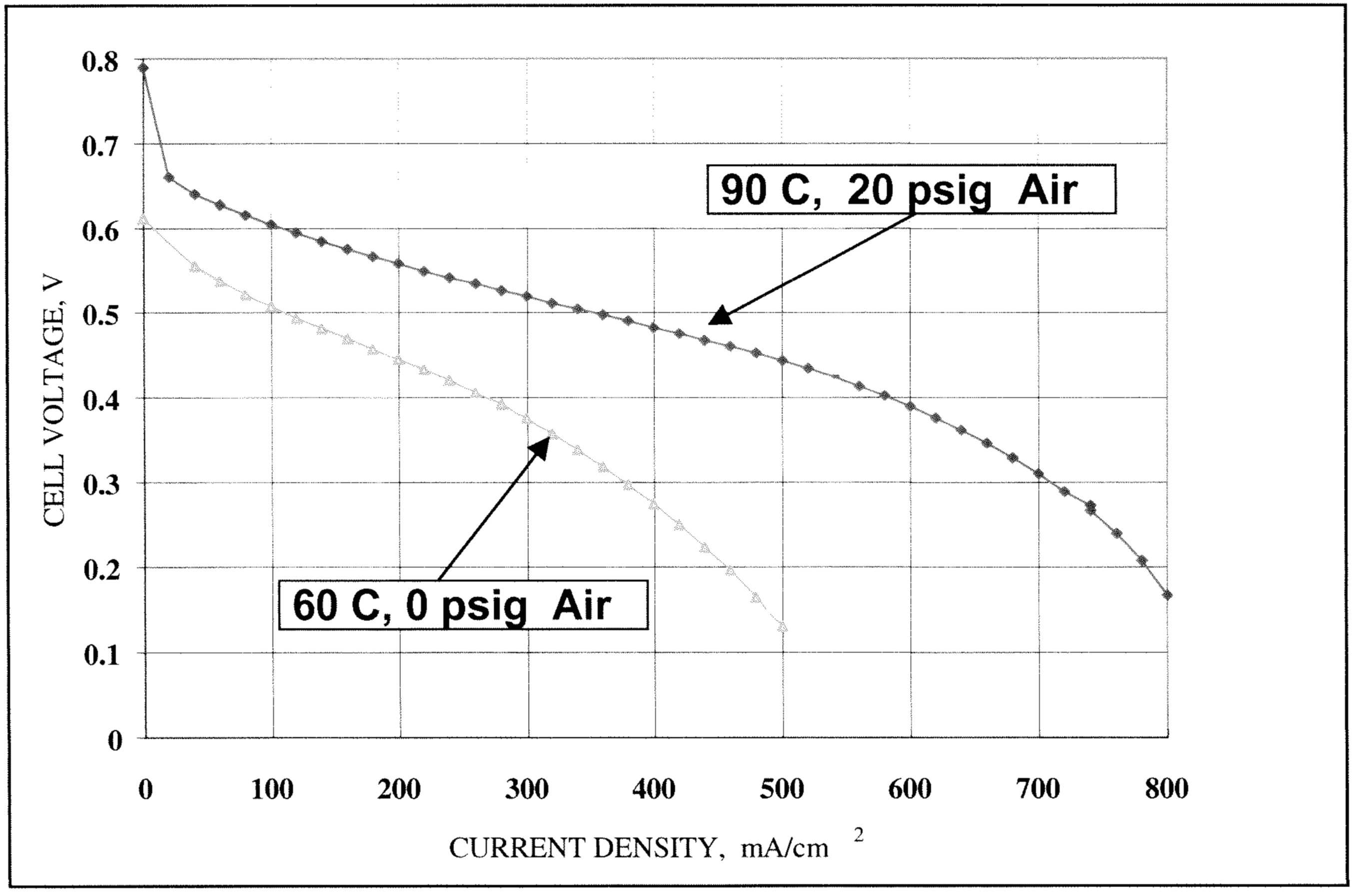
- **Aqueous -Liquid Feed DMFC**
  - Effective Heat Removal
  - More uniform stack temperature
  - Reduced Complexity of Stack design
  - No membrane dry out issues
- **Direct Oxidation**
  - Reduces System Parts count and weight
  - Reduces Control complexity



LAYOUT OF A DIRECT METHANOL FUEL CELL SYSTEM

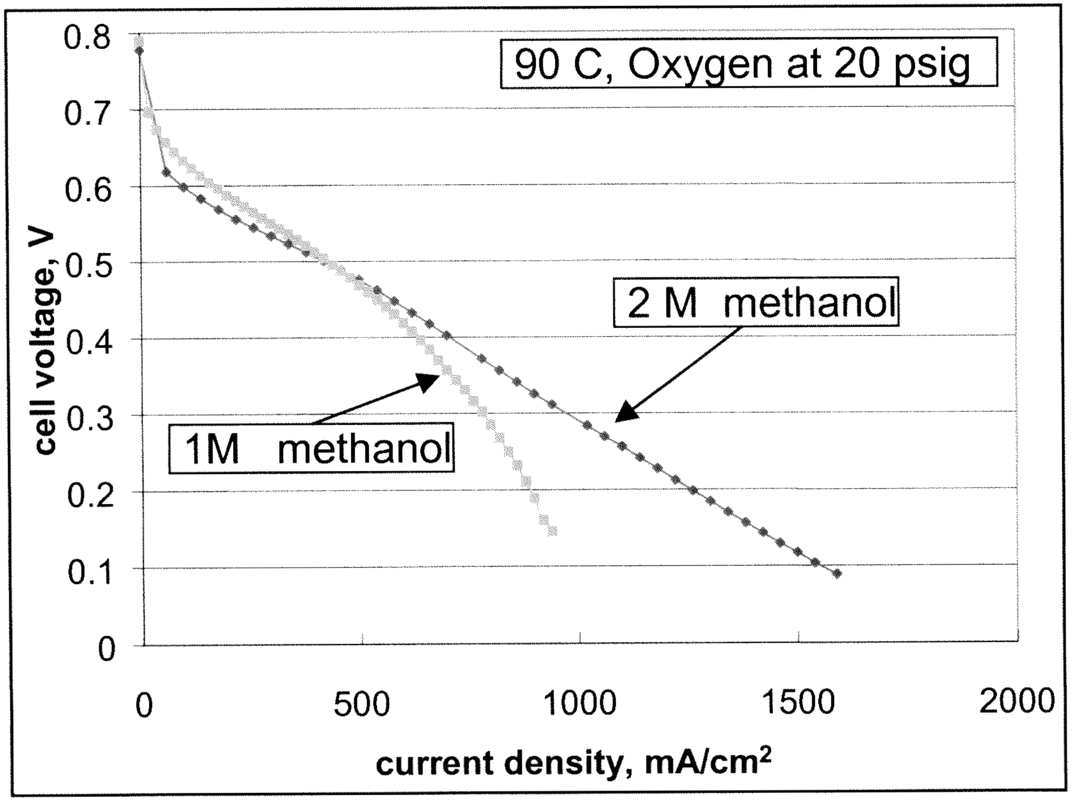


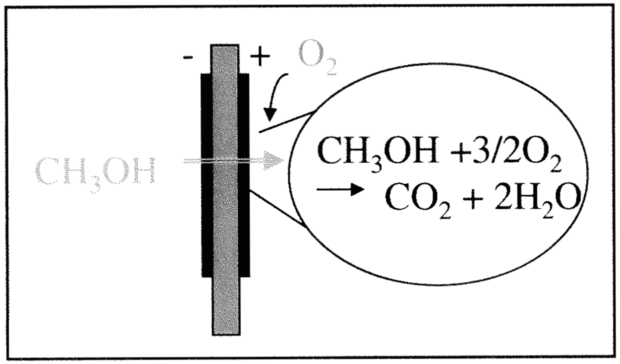
1M MeOH, DMFC ELECTRICAL PERFORMANCE



- 0.52 V at 300 mA/cm^2, 0.48 V at 400 mA/cm^2, Air 20 psig

CELL PERFORMANCE WITH INCREASED METHANOL CONCENTRATION





Concentration Of Methanol	Crossover Rate@ 90 C, 0.4 V, mA/cm2
1 M	85
2 M	176

• **Performance is higher. Crossover rate also higher**

ELECTROCHEMICAL FACTORS RELEVANT TO SYSTEM PERFORMANCE

SYSTEM PERFORMANCE CHARACTERISTICS	ELECTROCHEMICAL FACTORS
Power Density, W/Kg, W/L • Stack Mass • Balance of Plant Mass **Efficiency** • Stack Heat generation processes • Energy required by mass movement equipment • Energy required by rejection devices • Energy required power conditioning equipment **Load handling capability** • Reactant/Product concentration deviations caused by load • Response mechanisms for coping with changes **Environment –System sensitivity** • Response to temperature, humidity and pressure changes **Operating life** • Stable operation for desired periods	**Power Density, mW/cm^2** (operating point on V-I curve) • Catalytic activity (Pt-Ru, ...) • Ionic conductivity (Nafion, ...) • Electrode/ MEA characteristics **Reactant and Product Mass Transfer** • Concentration (Methanol Molarity) • Pressure (Air) • Flow rates (Relative to stoichiometric) • Temperature • Humidity • Flow field design features **Water handling through the stack** • Electro-osmotic transport (membrane type) • Temperature of operation **Heat generation processes** • Irreversibility (Deviation from Thermoneutral potential) • Crossover Rate (parasitic heat generation) **Degenerative processes** • Short term stability (for. e.g. flooding, dry out) • Long term irreversible loss (catalyst poisoning , membrane degradation)

CROSSOVER RATE MEASUREMENTS

- In line CO_2 Analyzer; Horiba VIA-550
- Calculation
  - Convert CO_2 Volume % into a volume flow rate of CO_2.
  - Use Ideal Gas Law to calculate a mole of CO_2/sec value.

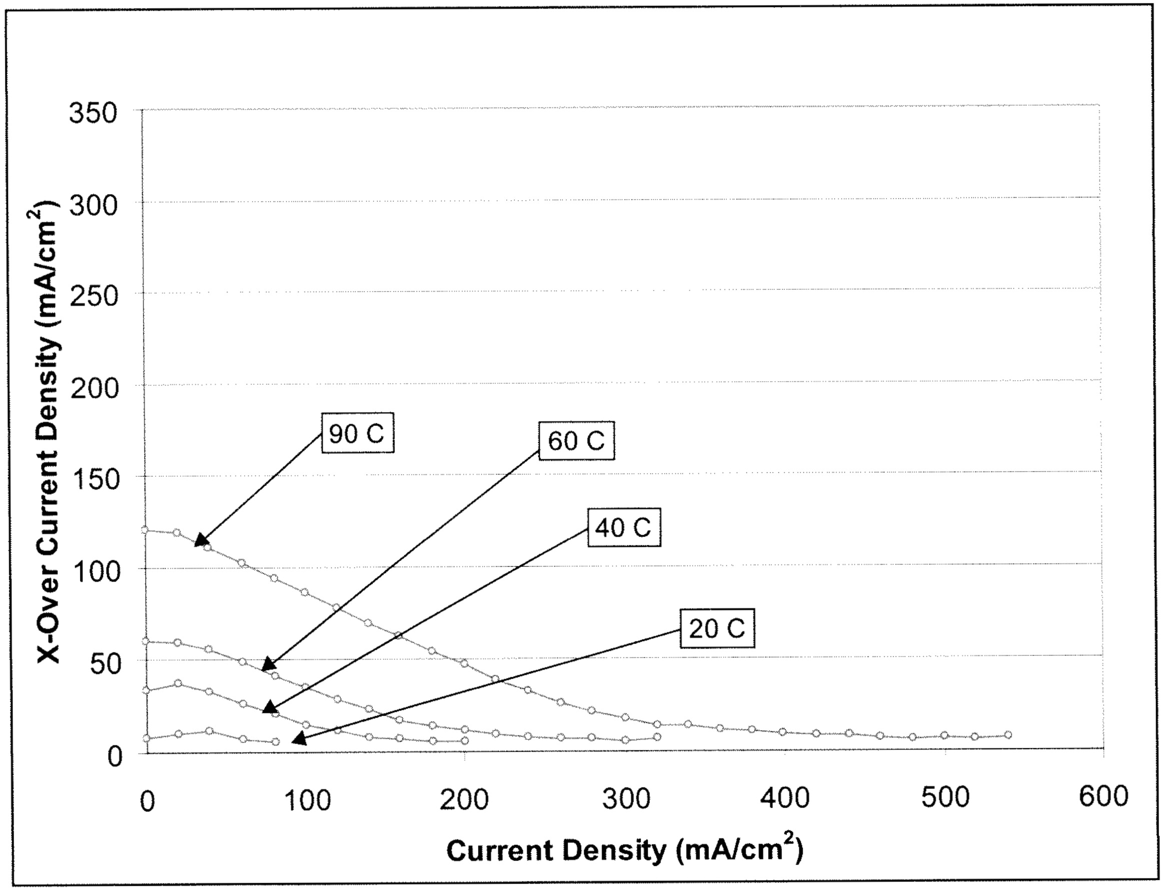
$$n = PV/RT \quad (1)$$

  - Use Faraday's Law to calculate an effective current which can be normalized into a current density.

$$I = n\, Fn_e \quad (2)$$

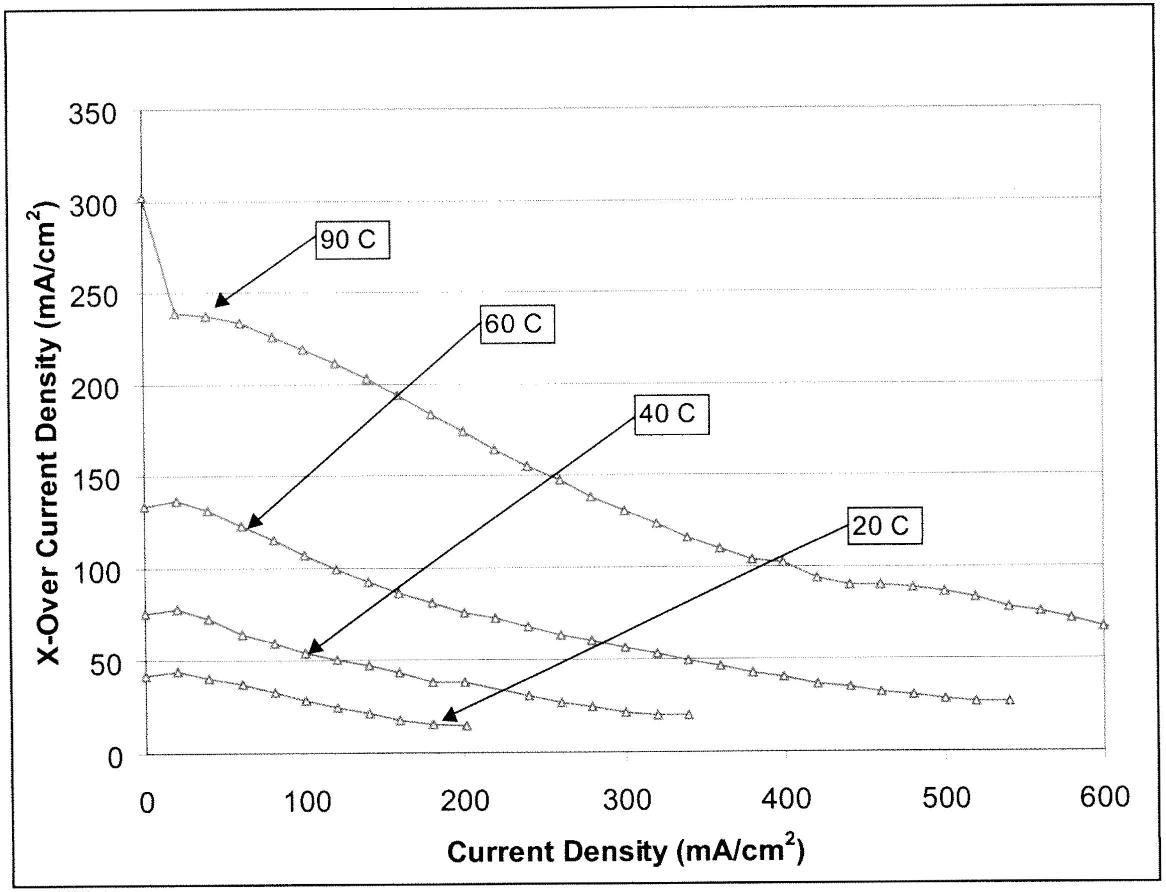
- Advantages of this method
  - Can see the effects of anode methanol consumption on crossover.
  - Is a true reflection of the CO_2 production in an operating cell.

CROSSOVER TEST, 0.5M MeOH



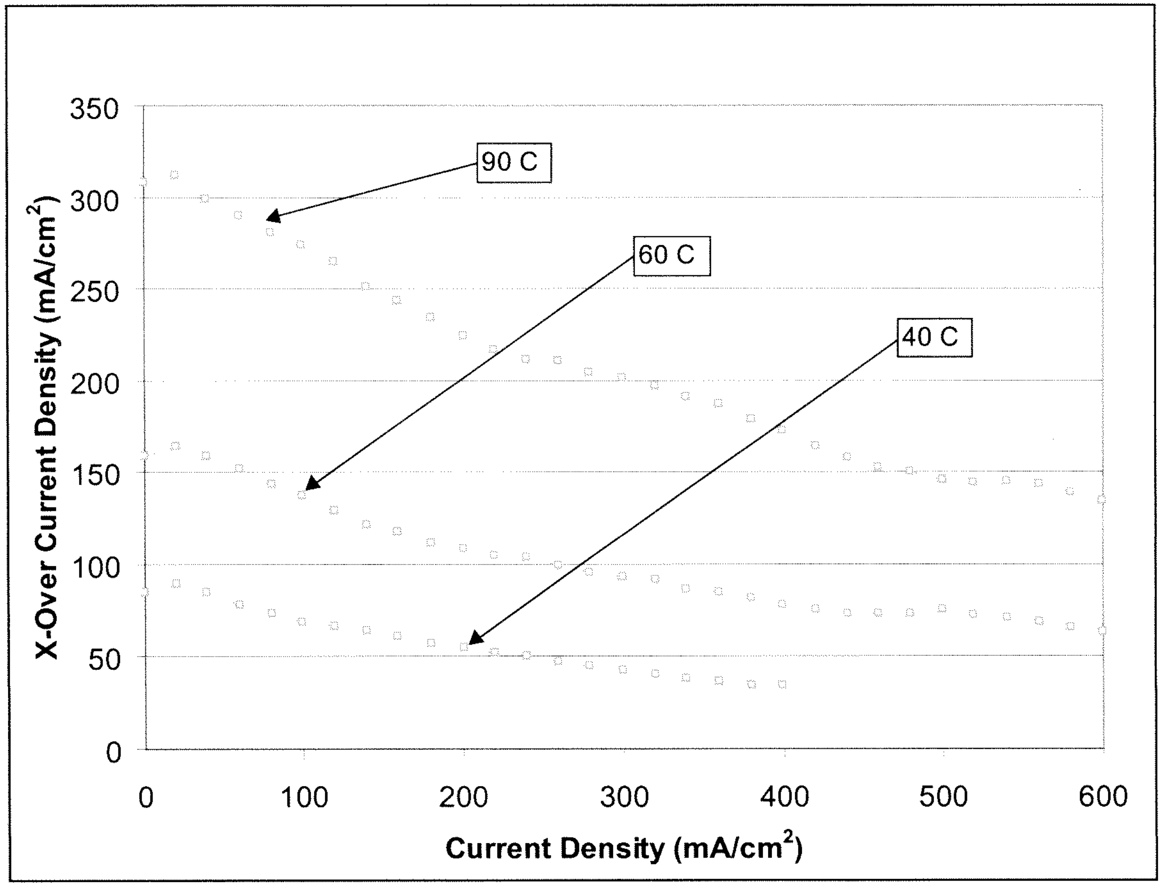
• **Crossover Current Density Increases With Temperature.**

CROSSOVER TEST, 1.0M MeOH



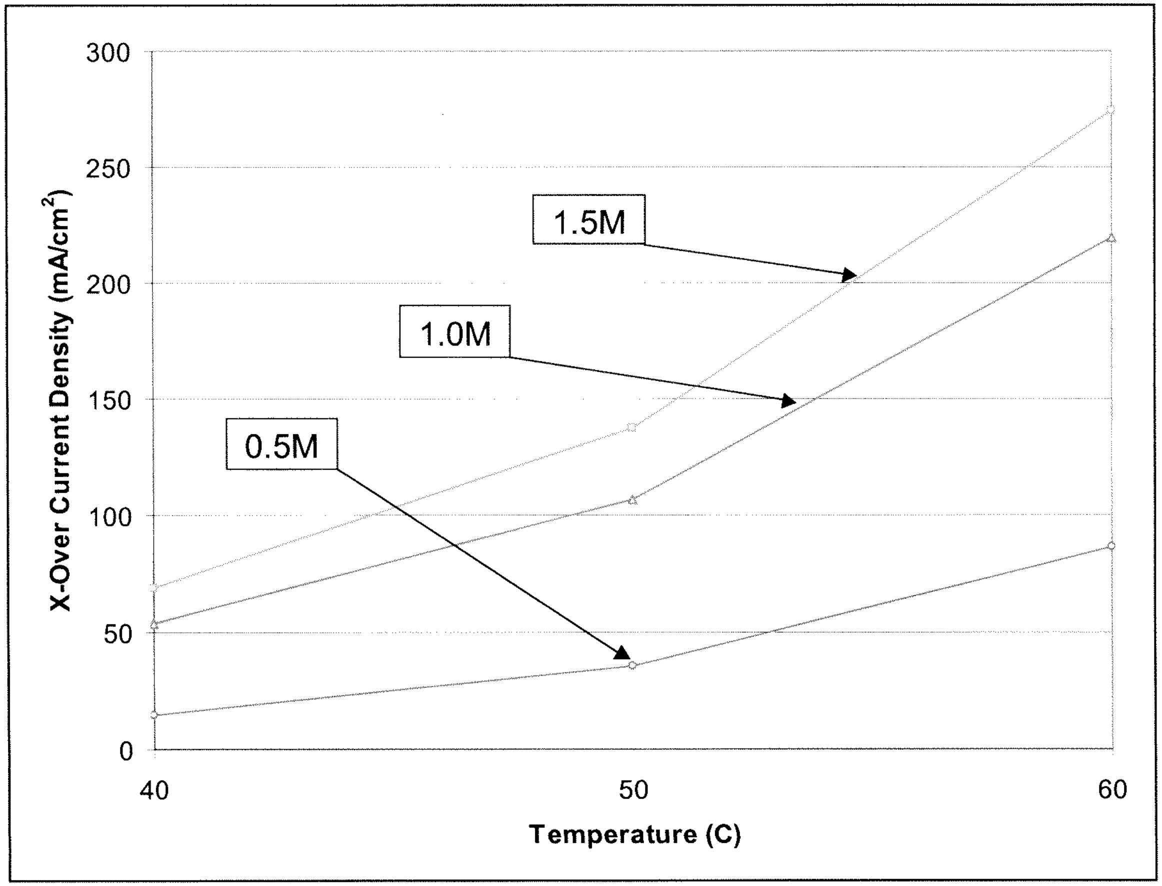
• **Crossover Current Density Decreases With Applied Current Density.**

CROSSOVER TEST, 1.5M MeOH



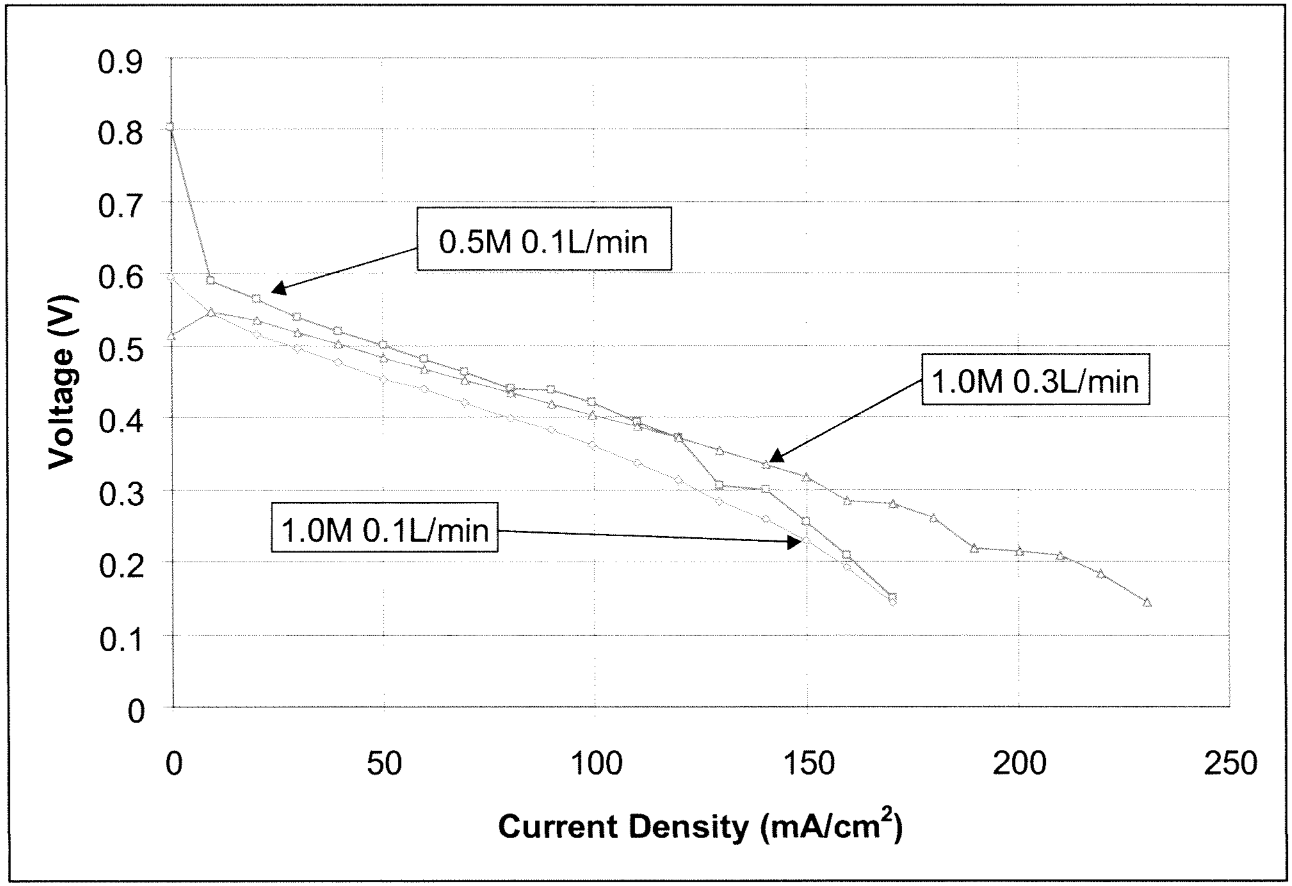
• **Crossover Current Density Increases With Methanol Concentration.**

CROSSOVER TEST, 100 mA/cm^2



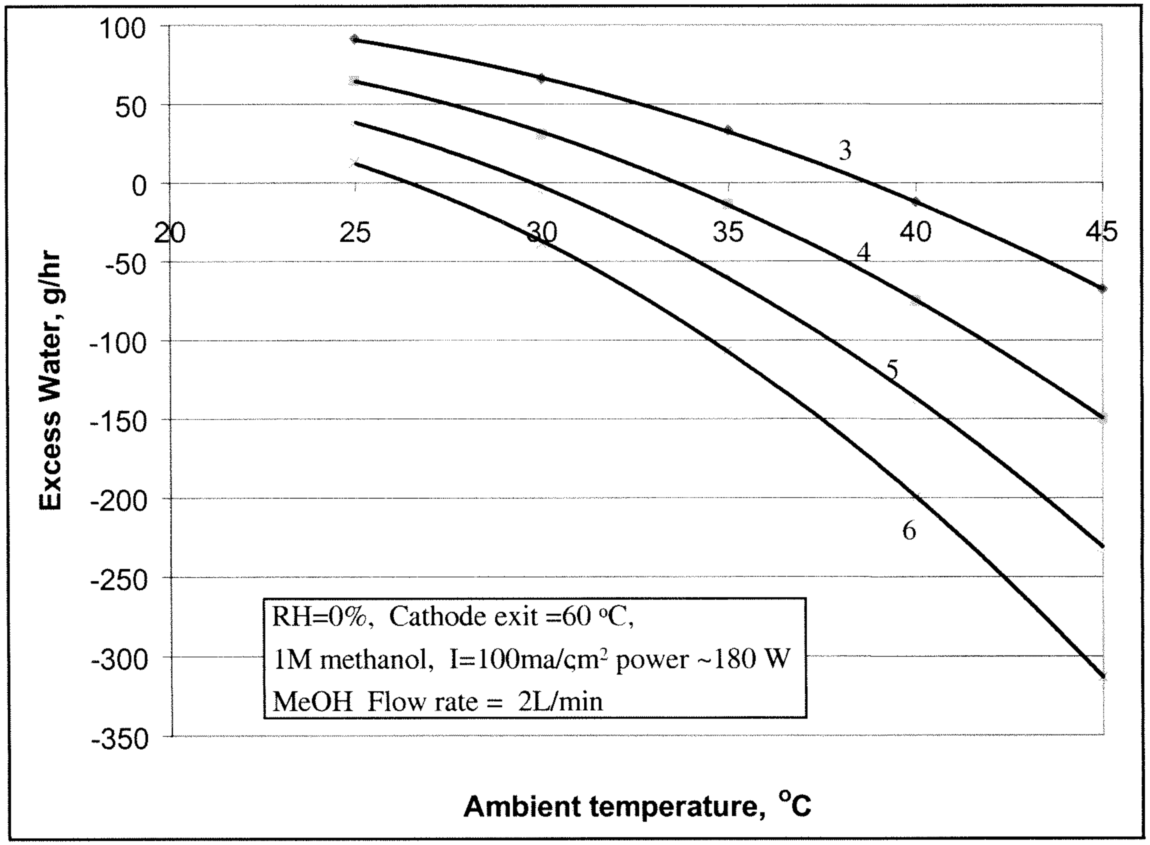
- **Crossover Current Density Increases With Temperature and Methanol Molarity.**

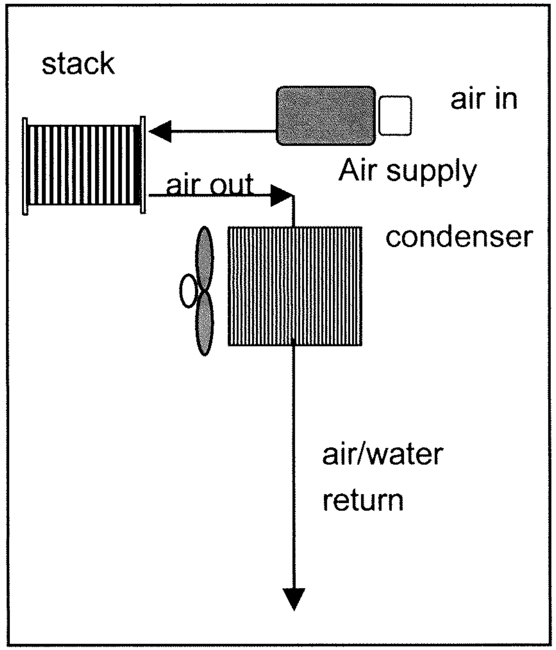
IV PERFORMANCE, 60C MeOH



- Molarity has a greater impact on DMFC performance than airflow rate.

EXCESS WATER RECOVERY AND ITS DEPENDENCE ON STOICHIOMETRY





- **WATER BALANCE CANNOT BE ACHIEVED WITH A CONDENSER AT HIGH STOICHIOMETRY, > 37°C AMBIENT**

IMPACT OF CONDENSER DUTY ON SYSTEM SIZE AND WEIGHT

- Condensing equipment are heavy (200Wth/kg)
- Air moving equipment require power (1We/25Wth)
- Allowance for air flow through condensers
  - increased system volume
- Water handling and return
  - pumps, valves, controls, additional power demand
- IDEALLY A CONDENSER IS TO BE AVOIDED
  - Possible if the stack can be operated at very low air flow stoichiometry.

ANODE POLARIZATION SUBTRACTION

- **Polarization Analysis**
  - Ecell, at any air flow rate, can be added to Ea at the same molarity and temperature to get Ec corresponding to the flow rate.

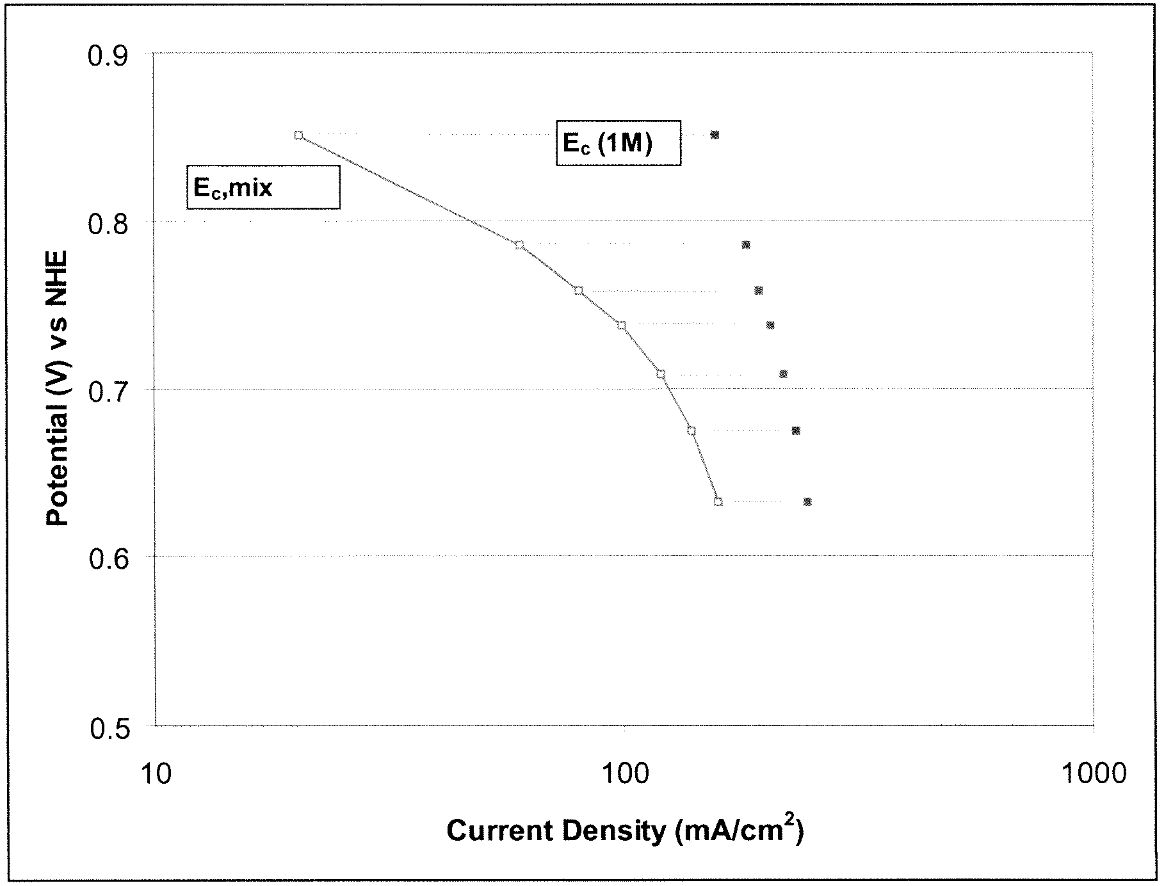
$$E_c = E_{cell} + E_a \quad (1)$$

  - When E_a and E_c are plotted together as a function of current density, the kinetics of the reaction can be seen.
- **Cathode performance correction**
  - The volume percent of CO_2 produced at the anode can be converted into an equivalent current, I_{cr}.
  - The total current applied to the cathode becomes:

$$I_{true} = I_{app} + I_{cr} \quad (4).$$

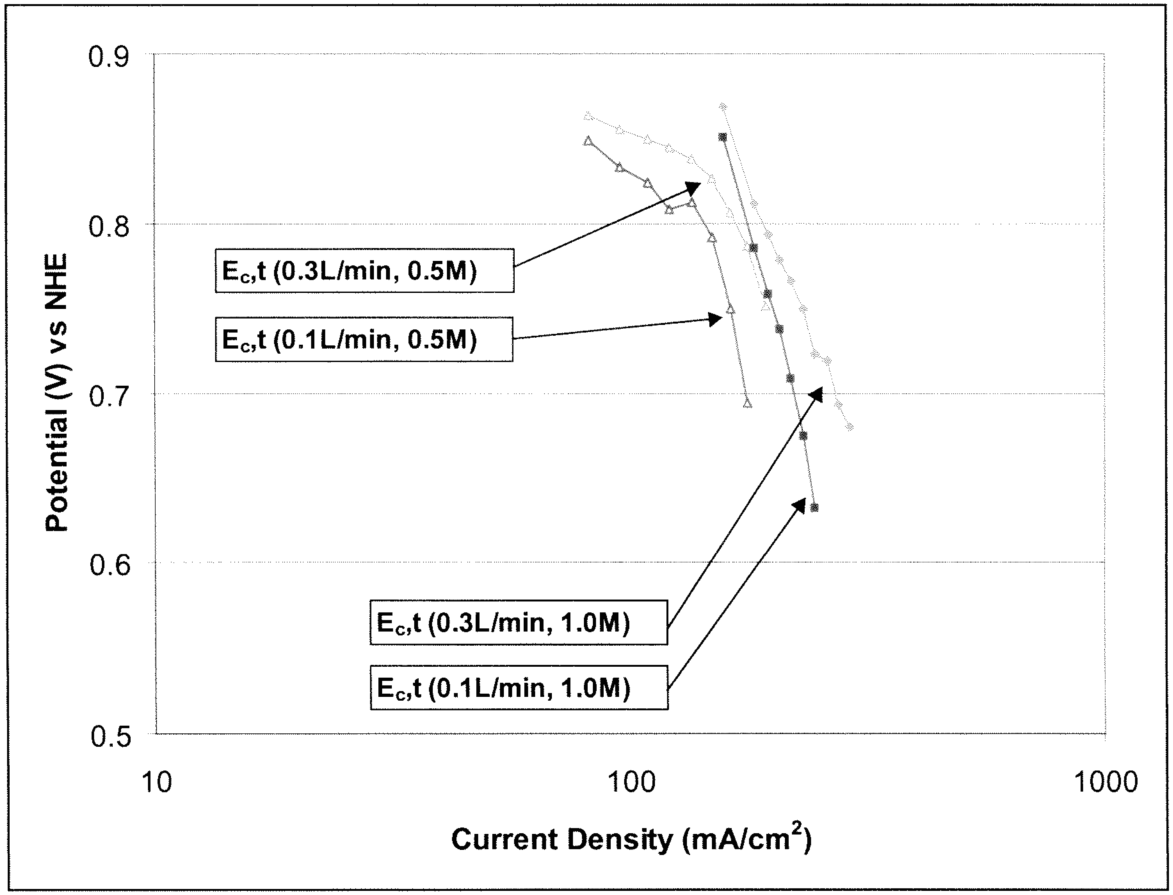
  Now E_c, mix can simply be called E_c.
  - E_c should be a constant regardless of methanol molarity.

CATHODE POTENTIALS, 60C, 0.1 L/min, AIR



- The DMFC cathode is starved for O_2, when operating on 1M MeOH.

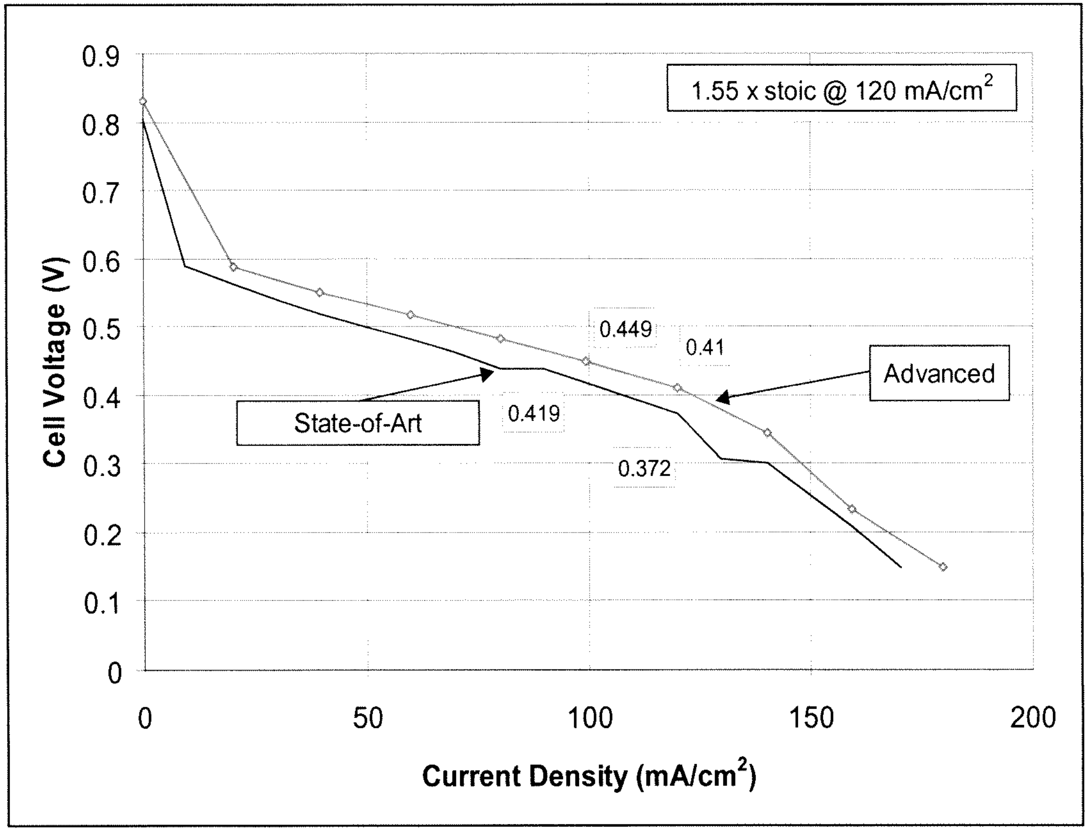
TRUE CATHODE POTENTIALS, 60C



• 1.0M Methanol in O_2 mass transfer limited regime regardless of airflow.

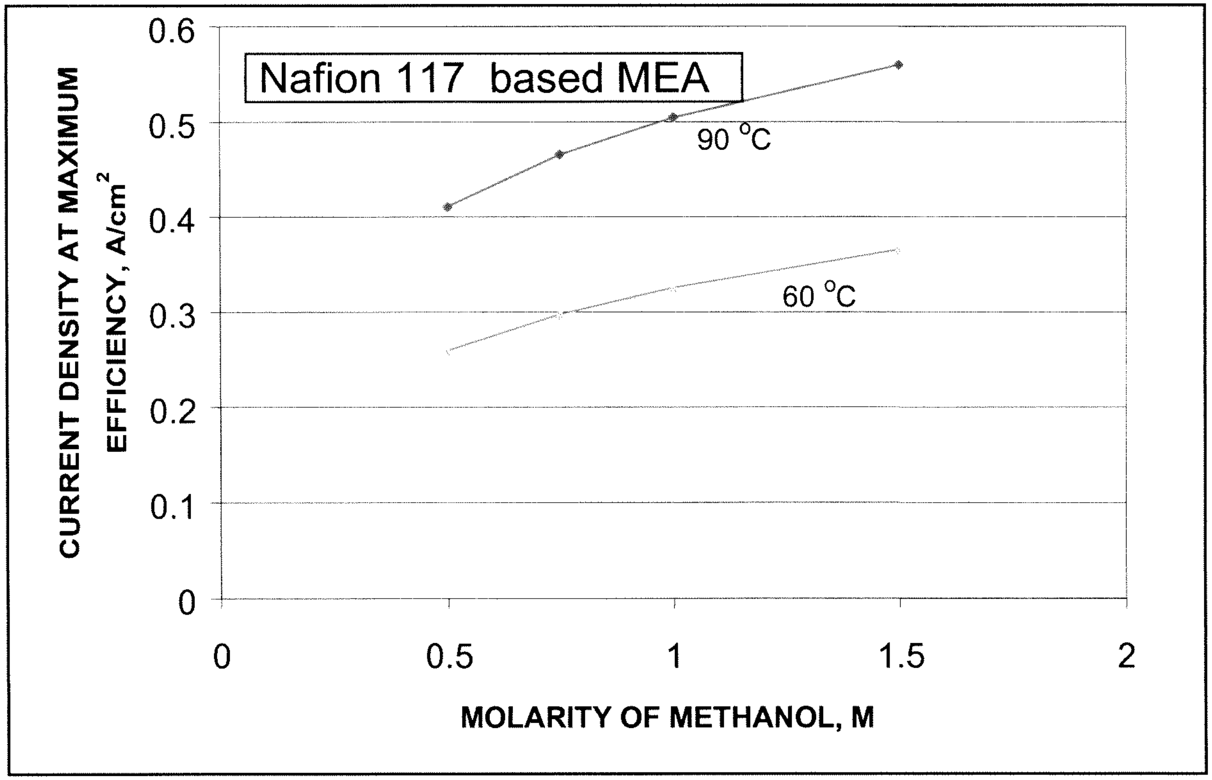
JPL

IV COMPARISON 60C, 0.5M MeOH, 0.1 L/min, AMBIENT AIR



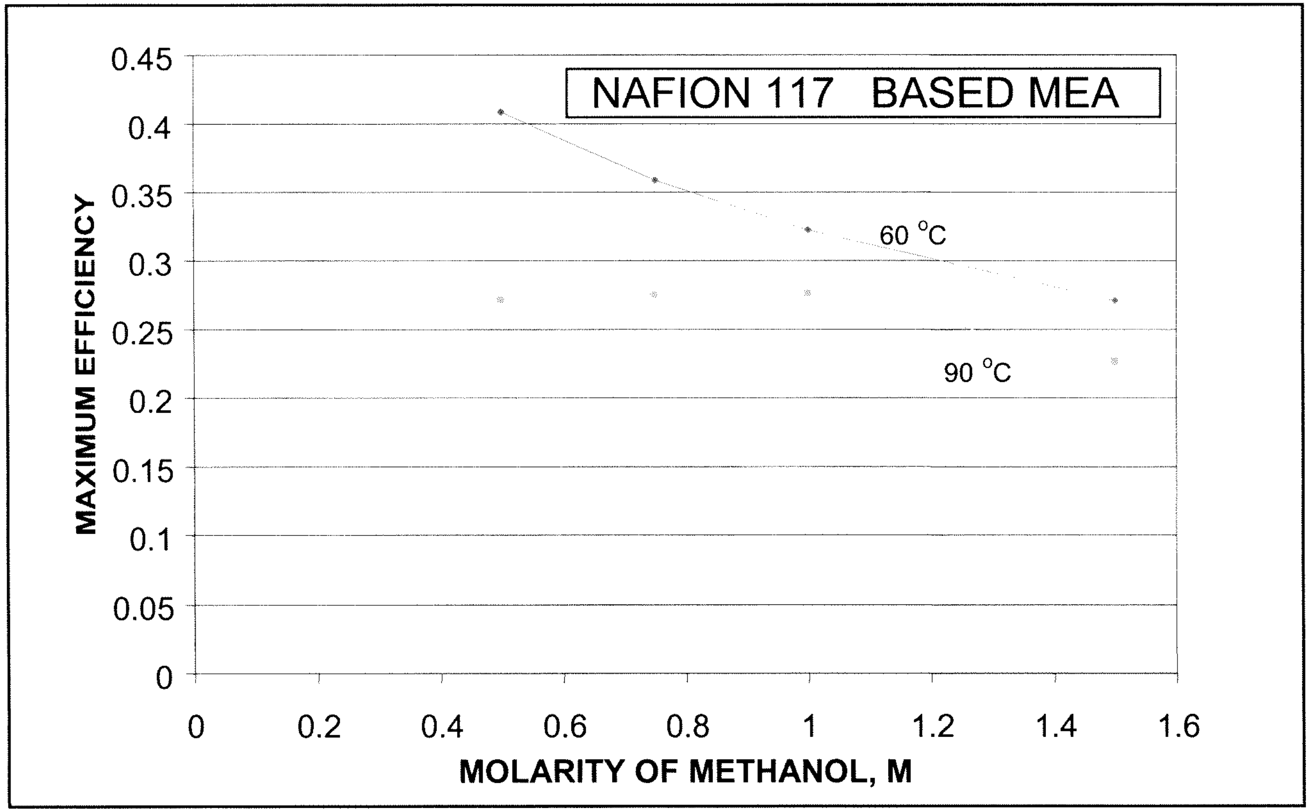
• **A 30mV at 100 mA/cm^2 improvement can be achieved with a novel cathode structure.**

THE CURRENT DENSITY ATTAINED AT MAXIMUM EFFICIENCY



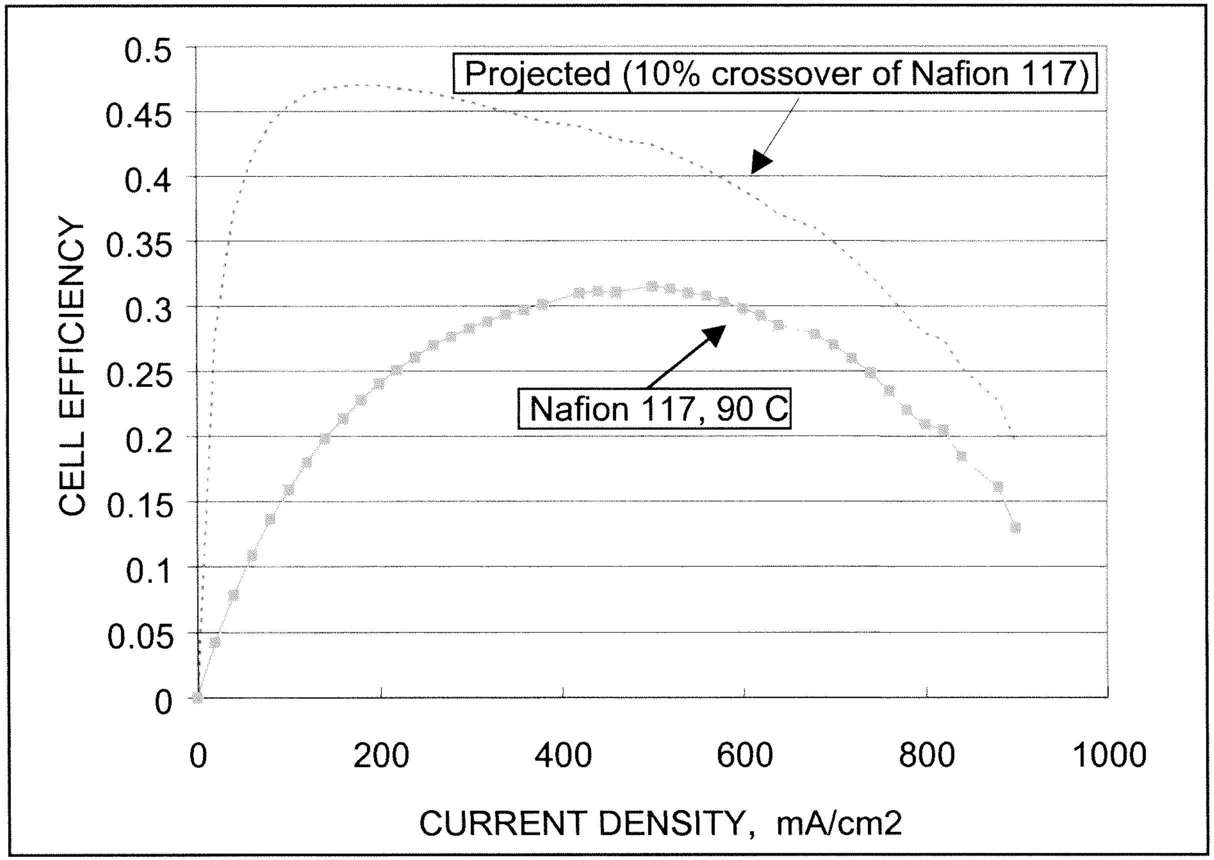
- **Current density at maximum efficiency point increases with temperature and concentration**

EFFECT OF CROSSOVER AND TEMPERATURE ON MAXIMUM EFFICIENCY



- **Maximum efficiency decreases with increasing temperature at all molarities**

PROJECTED IMPROVEMENT IN EFFICIENCY WITH LOW CROSSOVER MEMBRANES



•Efficiencies greater than 40% are projected with membranes exhibiting low methanol crossover

SUMMARY

- **System Performance sensitivity very high to**
  - **air flow rate**
  - **concentration of methanol**
- **Air flow rate performance 1.5-1.75 x stoic**
  - **essential to avoid water recovery**
  - **extend temperature range of operation**
- **Operation at lower stack temperatures(60°C)**
  - **Will lead to higher system performance**
- **Concentration control necessary to achieve good system stability**
  - **viable methanol concentration sensor demonstrated**

Acknowledgements

- DARPA-DSO
- NASA- JPL, Caltech